RAW MATERIALS

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KAOLINS FOR PRODUCTION OF SANITARY CERAMICS

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Several types of kaolins from different manufacturers were investigated. The chemical, mineral, and granulometric compositions of the kaolins and their effect on the properties of the finished pastes were investigated. The properties of kaolins required for optimizing the properties of ceramic pastes were determined. The rheological characteristics were examined and their effect on control of the manufacturing process were examined. The basic drawbacks and advantages of the different types of kaolins, both those traditionally used by domestic manufacturers and some new ones, were established.

Production of sanitary ceramic articles is now increasing significantly. New factories are being built and old ones are being modernized. Introducing new technologies and equipment, improving product quality, and increasing labor productivity are the problems that manufacturers of sanitary ceramics now face. Studying and selecting raw materials and using them to create pastes that would ensure highly efficient production are a pressing problem in this respect.

Manufacturing the intermediate product in a plaster mold in traditional casting and in casting in polymer molds under medium and high pressure is the main limiting stage in production of sanitary ceramics. Reducing the time for obtaining the cast will allow increasing labor productivity and thus more efficiently utilizing the equipment. Clays and kaolins are the basic raw material in production of sanitary and industrial articles which are contained in slips and significant affect their process properties, including filtration.

We performed a comparative analysis of the properties of kaolins, both those traditionally used in Russian companies, and kaolins from some European manufacturers. The basic manufacturers of kaolins in Europe are located in England, France, Germany, and the Czech Republic. Ukrainian kaolins are traditionally offered on the domestic market. Kaolins from Russian deposits located in the Urals (Chelyabinsk oblast) are stimulating great interest.

One serious problem in the ceramics industry is the lack of high-quality raw materials. Until 1999, Prosyanovsk and Glukhovetsk kaolins covered 70% of the demand for kaolin. Only one deposit – Zhuravlinyi Log (Chelyabinsk oblast) – could compete with Ukrainian kaolins. It should be acknowledged that this deposit, combined with effective extraction technology, concentration of the raw material, and constant finished product quality control, is now almost the only domestic source of kaolin concentrate. Today the basic consumers of enriched kaolin from Plast-Rifei Co. are porcelain and ceramic factories. Worldwide, 40 million tons of kaolins are extracted, and enriched kaolins are basically used. The leading manufacturers are the USA, Great Britain, and Australia. In Russia, 505,000 tons of kaolin clays is extracted, and 30,000 tons is concentrated [1, 2].

We investigated a large number of types and brands of kaolins from different manufacturers, but kaolins currently on the Russian market were selected for analysis: KZhF-2 from Plast-Rifei Co. (Russia), Glukhovetsk KS-1 (Ukraine), Prosyanovsk KS-1 (Ukraine), Sedleckiy MK-2 (Czech Republic), AL SOKA (France), CC-31 WBB (Great Britain).

Many factors affect the properties of slips, including the chemical composition and the mineral composition and dispersion of the raw material components. The chemical and mineral compositions of clay raw materials are responsible for the refractoriness, mechanical strength, thermal stability, moisture resistance, and other properties of ceramic materials on which the reliability, stability, and lifetime of ceramic articles in different conditions of use are dependent. The suitability of clays for production of ceramic articles is determined by their physical and technical properties (molding, drying, firing) which are caused by their plasticity, liquescence of suspensions by electrolytes, sensitivity to drying, tendency to cake, phase changes and transitions which the clays undergo during firing, and other properties. In turn, these properties of clays are predetermined by their mineral

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TABLE 1

Kaolin	Mass content, %									Concentration, mg/kg			
	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	K_2O	Na_2O	calcination loss	Ca^{2+}	Mg^{2+}	chlorides	sulfates
KZhF-2 (Plast-Rifei Co.)	46.80	36.75	0.79	0.64	0.78	0.23	0.43	0.11	13.46	110	28	41	212
KS-1 (Prosyanovsk)	47.67	36.65	0.54	0.78	0.49	0.10	0.82	0.04	12.92	210	52	173	777
KS-1 (Glukhovetsk)	47.68	37.20	0.50	0.52	0.24	0.08	1.21	0.03	12.54	73	16	17	50
MK-2 (Sedleckiy)	51.02	34.17	1.29	0.38	0.12	0.20	1.68	0.10	11.04	99	14	15	278
CC-31 (WBB)	47.60	34.30	0.60	0.03	–	0.30	2.30	0.05	11.00	–	–	–	–
AL (SOKA)	48.20	35.80	0.98	0.40	1.54	0.70	1.40	0.10	12.40	50	10	17	270

composition, dispersion, the morphology of the clay particles, and the composition of impurities [3].

The most important constituent of clays is alumina, Al_2O_3. It has the greatest effect on the properties of ceramic articles. The refractoriness and mechanical strength of ceramic materials increase with an increase in the Al_2O_3 content, a significant fraction of the chemical composition of kaolins (from 8 to 40% and higher). It should be noted that the plasticity of ceramic paste and shrinkage (the drying and firing conditions improve) decrease in significant quantities of SiO_2 on one hand, and the refractoriness decreases on the other.

The most severe requirements are imposed on the content of coloring oxides – iron and titanium. With an excess of these compounds, porcelain or faience turn red, brown, yellow, and light purple, while manganese oxides impart orange and black coloring. As a function of the ratio of these impurities in the clays, the articles also acquire different colors, for example, light brown and dark yellow if the ratio of $Fe_2O_3 : CaO = 0.6 – 0.8$ and bright yellow and yellow if $Fe_2O_3 : CaO < 0.5 – 0.6$. In addition, if the kaolin contains iron in the free state, it can appear on the surface of articles as dark dots, so-called "specks." Studies at the Scientific-Research Institute of Physics showed that increasing the total coloring oxide content in porcelain ($Fe_2O_3 + TiO_2$) by even 0.1% decreases the whiteness by approximately 3%. Iron and titanium oxides are strong fluxes that reduce the viscosity of the liquid phase and the agglomeration range; in addition, they decrease the mechanical strength. Calcium oxide, frequently encountered in kaolins, acts as a flux. The negative effect of this oxide is manifested by worsening of the structural and mechanical properties of kaolin and by an increase in instability and decrease in slip fluidity and liquescence [4].

The presence of water-soluble salts, especially calcium, magnesium, or iron sulfates, and chloride salts in the clays decrease the diluting power of water glass. In some clay varieties, the calcium and magnesium content in terms of oxides attains 25%, but the total content is usually no greater than 5 – 10%. Many studies have shown that water-soluble salts can be removed by two methods: by filter pressing and by adding barium carbonate or hydroxide to the slip to convert the sulfate into difficultly soluble $BaSO_4$ salt [5, 6].

Particulate contaminants, primarily free quartz sand in the form of relatively large grains and undecomposed rock contaminant residues significantly decrease the plasticity of the ceramic paste. In addition, large contaminant particles perturb the homogeneity of the paste and increase the caking temperature and crack formation.

All mined kaolins are concentrated to remove undesirable inclusions. The concentration methods are based on different physical and chemical properties of the constituents of the raw material – density, wettability, solubility, magnetic susceptibility, etc. Selection of the concentration method is determined by the properties, requirements for the concentrated raw material, production volume, and other factors. This can be manual sorting, sieving on sieves, washing in pans or in washing drums, air separation, flotation, etc. [7].

Let us examine some data on the compositions of these kaolins. The chemical composition was analyzed by x-ray fluorescence analysis (Philips system). Solutions of kaolins (solid substance : water = 1 : 10) were also prepared and the soluble salt content and presence of sulfates and chlorides were tested. The results of the analyses are reported in Table 1.

KZhF-2, KS-1 (Prosyanovsk) and KS-1 (Glukhovetsk) kaolins have similar chemical compositions. MK-2 and AL kaolins have a totally different composition. They contain more SiO_2, K_2O, and Fe_2O_3 and less Al_2O_3. A high K_2O content is a positive factor, since it decreases the feldspar content – the most expensive component for standard pastes for sanitary and industrial articles – in the finished paste.

The concentration of soluble salts is different in different types of kaolins. KS-1 (Glukhovetsk) kaolin has few contaminants, while KS-1 (Prosyanovsk), MK-2, and AL kaolins on the contrary contain more contaminants. There are especially many in KS-1 (Prosyanovsk) kaolin. It contains a very large quantity of sulfates, chlorides, and soluble Ca^{2+} and Mg^{2+} salts. The high coagulant ion content in KS-1 (Prosyanovsk) kaolin sharply increases the viscosity of the finished slip and consequently the electrolyte content in the paste, so that it is difficult to use in pure form. The casting properties of slips with KS-1 (Prosyanovsk) kaolin can be improved by using the so-called press method, i.e., by filter pressing and subsequent melting of the filter cakes. The effect attained is due to removal of most of the coagulant ions contained in the sorption complex of the initial kaolin during filtration.

In addition to the chemical composition, especially of clays and kaolins, it is important to know the phase composition of the minerals to develop the composition of the ce-

TABLE 2

Kaolin	Mass content, %, mineral phases			
	feldspar	quartz	muscovite	kaolinite
KS-1 (Prosyanovsk)	1	3	5	91
KS-1 (Glukhovetsk)	2	4	10	84
KZhF-2 (Plast-Rifei Co.)	1	4	6	89
MK-2 (Sedleckiy)	1	11	15	73
CC-31 (WBB)	8	1	11	79
AL (SOKA)	3	3	10	84

ramic paste. The mineral composition of the argillaceous raw material is an important index that determines the features of its structure formation and properties. Minerals form chemical compounds of homogeneous structure, composition, and properties. Clays consist of basic clay-forming minerals and contaminant minerals. The basic clay-forming minerals include kaolinite, montomorillonite, and hydromica [8].

X-ray diffractometry was used to analyze the mineral composition of the kaolins (Table 2). All types of kaolins contain kaolinite as the basic clay-forming mineral. The highest content is in KS-1 (Prosyanovsk) kaolin. MK-2 kaolin is distinguished by a high quartz and muscovite content, and a high feldspar content is characteristic of kaolin CC-31, which also explains the high K_2O content.

Argillaceous rocks consist of particles of different size. The most valuable for ceramics production are the fine clay fractions with a grain size of less than 0.5 – 1.0 μm, which increases the reactivity of the clays in firing and other processes. Kaolin particles are very small and have a laminar structure so that they can fit closely together. The granulometric composition of the different types of kaolins can differ sharply [9].

In studying the granulometric composition of the kaolins, a series of sedimentation analyses was performed on a SediGraph 5100 (see Fig. 1). Kaolins KS-1 (Prosyanovsk), KS-1 (Glukhovetsk), and KZhF-2 have almost the same granulometric composition and are highly disperse. Kaolin CC-31 has a lower content of particles less than 5 μm in size. It should also be noted that kaolin MK-2 was the coarsest and kaolin AL had low dispersion and was in the middle of all of the materials investigated.

Such a property of kaolins as liquescence is the most important for production of articles by casting as it is responsible for decreasing the moisture content and retaining sufficient slip mobility in mold filling due to incorporation of diluting electrolytes in the slip. This favors their reaction with the suspension, which has the basic properties of colloidal systems and the capacity for exchange reactions and sorption of water.

Slip suspension must have the following properties for quality molding by casting and obtaining relatively dense casts with satisfactory strength and a good surface:

low viscosity, required for totally filling molds, especially of complex configurations, and for transporting the slip to the casting sites; it is also desirable for the viscosity to change as little as possible in time;

high aggregate and sedimentation stability, which causes casting systems not to separate during storage before molding and during shipment;

a high concentration of solid phase, which usually ensures obtaining denser casts and lower shrinkage in drying and firing, which in turn prevents crack formation and deformation; in addition, for low cast moisture content, less time and thermal energy are required for drying intermediate products;

ability to ensure cast formation on the surface of a plaster mold which has high filtering characteristics to increase the productivity of the casting process.

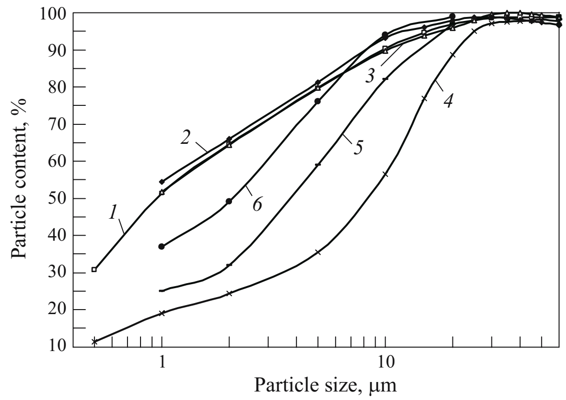

Fig. 1. Granulometric composition of kaolins: *1*) KS-1 (Prosyanovsk); *2*) KS-1 (Glukhovetsk); *3*) KZhF-2 (Plast-Rifei Co.); *4*) MK-2 (Sedleckiy); *5*) AL (SOKA); *6*) CC-31 (WBB).

The analysis of these requirements shows their contradictory character, and they would be mutually exclusive. For example, at a high concentration of solid phase in the suspension, sedimentation stability can be attained, but the aggregative stability will decrease and the viscosity will increase. For this reason, it is not possible to obtain better indexes to the full degree, and optimization of all slip properties to a satisfactory level is usually the goal.

Plastic materials strongly affect the rheological properties of casting slip. Measurements of the rheological properties of the suspension are the final evaluations in determining the physical and chemical properties of argillaceous raw material. These measurements allow predicting the properties of the slip and can be used for controlling the manufacturing process in production of slips.

Lots of slip referring to 500 g of dry solid were taken to study liquescence. Before the test, the slip was held for a minimum of 16 h. The studies were conducted on a viscometer with Gallenkamp coaxial cylinders. The angle of rotation was measured immediately after pouring the slip and then 10 min later.

The following properties were studied separately: density, viscosity, and Gallenkamp thixotropy, cast formation

TABLE 3

Kaolin-based slip*	Amount of electrolyte, %	Gallenkamp angle of rotation, deg			Hardening time, min–sec	Collected body thickness after 60 min, mm
		immediately	after 10 min	difference		
KS-1 (Glukhovetsk)	0.150	312	206	160	11 – 30	13.5
	0.175	241	295	46	2 – 00	9.2
	0.200	350	335	15	1 – 50	8.0
	0.225	352	350	2	1 – 25	6.8
KZhF-2 (Plast-Rifei Co.)	0.375	345	310	35	3	11.9
	0.400	352	324	28	3	10.5
	0.425	350	336	14	3	9.5
	0.450	354	345	9	3	9.5
KS-1 (Prosyanovsk)	0.675	343	317	26	2 – 25	7.8
	0.700	347	330	17	1 – 50	7.6
	0.725	350	343	7	1 – 30	8.3
	0.750	349	340	9	1 – 25	7.3
MK-2 (Sedleckiy)	0.250	332	305	27	1 – 30	21.3
	0.275	330	325	5	1 – 30	18.8
	0.300	334	334	0	1 – 30	17.3
	0.325	340	340	0	1 – 30	16.4
AL (SOKA)	0.275	340	300	40	2 – 50	17.0
	0.300	345	325	20	1 – 50	14.4
	0.325	345	340	5	1 – 50	11.5
	0.350	350	350	0	1 – 30	11.0
CC-31 (WBB)	0.075	310	280	40	2 – 30	14.7
	0.100	330	305	25	2 – 30	13.3
	0.125	350	340	10	2 – 30	11.8
	0.150	350	350	5	2 – 30	11.0

* In all cases, the density was 1.6 g/cm^3 and the temperature was 22°C.

(mm/60 min), hardening time (filtration properties), stability and properties in removing cast from mold.

The studies on cast formation were conducted on standard plaster molds from Kirov Stroifarfor Co. The results obtained are reported in Table 3.

The rheological characteristics of the kaolins differed significantly. Kaolin CC-31 can be distinguished in the comparison with the best indexes. The minimum amount of electrolyte required for attaining the optimum viscosity was characteristic of this kaolin; almost the same hardening time at different concentrations of electrolyte was observed, which is indicative of good filtration properties. Kaolin KS-1 (Glukhovetsk) also required an insignificant amount of electrolyte, but when the content was increased, the cast formation rate decreased. Kaolin KS-1 (Prosyanovsk) had the highest consumption of electrolyte and also the lowest cast aggregation rate. The high salt content had an effect here. The highest cast formation rate was also observed for kaolin MK-2, but the same hardening time indicates the good filtration power. Kaolin AL, with moderate electrolyte consumption, was also characterized by a high cast aggregation rate. Kaolin KZhF-2 had a moderate cast formation rate at sufficiently high electrolyte consumption and also differed in the same, but relatively long hardening time. As a consequence, this type of kaolin will not provide for a high rate of intermediate product output on modern equipment without addition of other kaolins.

TABLE 4

Kaolin	Bending strength, MPa	Shrinkage, %	Deformation, mm	Water absorption, %
KS-1 (Prosyanovsk)	1.80	11.7	5.0	10.5
KS-1 (Glukhovetsk)	0.50	11.3	8.5	9.9
KZhF-2 (Plast-Rifei Co.)	0.35	11.5	5.0	11.9
MK-2 (Sedleckiy)	1.00	7.0	10.5	27.2
AL (SOKA)	1.10	8.7	7.0	16.0
CC-31 (WBB)	1.30	13.0	5.5	8.5

To optimize the properties of ceramic paste, it is important to determine and analyze the physical properties of untreated (after drying) and fired samples of the raw materials. The flexural strength and shrinkage after drying were determined in unfired samples of kaolins. Samples were cast in the shape of rods. After firing at the maximum temperature of 1220°C, the deformation, firing shrinkage, and water absorption of the samples were determined (Table 4).

Kaolins KS-1 (Glukhovetsk) and KZhF-2 had low flexural strength in the dry state. For the other samples, these values were standard for concentrated kaolins. In comparing the ceramic properties, kaolin MK-2 stood out – it had the highest water absorption and lowest shrinkage and slightly higher deformation.

Most of these kaolins can thus be used for manufacturing the pastes used in production of sanitary and industrial ware.

The kaolins traditionally used in Russian firms – KS-1 (Prosyanovsk), KS-1 (Glukhovetsk), and KZhF-2 (Plast-Rifei Co.), however, do not have all of the necessary properties for creating pastes that ensure high processability and productivity in casting sanitary and industrial articles on modern equipment both in traditional casting in plaster molds and in high-pressure casting in polymer molds. The cause is the low filtration rate and high amount of electrolyte required for obtaining the optimum viscosity. However, combination with such kaolins as MK-2 and AL, which have good filtering power, makes it possible to improve the parameters of the finished slip and intensify the intermediate product production process. Kaolin CC-31 is optimized for fabrication of sanitary and industrial articles and satisfies the most severe requirements for creation of high-tech production. Its high cost will significantly affect production costs, which could affect the competitiveness of the finished product. For this reason, this type of kaolin should be used for correcting the composition of the pastes to improve their parameters, including for production of special kinds of articles.

The ceramics industry cannot grow if manufacturers are not provided with quality raw materials, which would mainly allow creating new technologies and manufacturing more complex articles with high quality and productivity indexes. Providing ceramics companies with domestic raw materials and revamping the process will reduce the cost of the articles and solve a major problem – becoming competitive with imported articles.

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